

CLAIMS

We claim:

1. A high pH aqueous based zirconium (IV) crosslinked guar fracturing fluid suitable for use in wells with bottom-hole static temperatures of 250°F or greater, comprising:

a polymer solution, comprising:

an aqueous fluid,

natural guar gum,

a stabilizer,

an alkaline buffer and

an alpha-hydroxycarboxylic acid delaying agent, and

a zirconium (IV) crosslinking agent.

2. The fracturing fluid according to claim 1, wherein the aqueous fluid comprises substantially any aqueous fluid that does not adversely react with one of the constituents of the fracturing fluid, the subterranean formation, and the fluids present therein.

3. The fracturing fluid according to claim 1, wherein the aqueous fluid is selected from the group consisting of fresh water, natural brines, and artificial brines.

4. The fracturing fluid according to claim 3, wherein the artificial brines are selected from the group consisting of potassium chloride solutions and sodium chlorides solutions.

5. The fracturing fluid according to claim 1, wherein the stabilizer comprises any free-radical-scavenging compound.

6. The fracturing fluid according to claim 1, wherein the stabilizer is selected from the group consisting of sodium thiosulfate, thiourea, urea, sodium sulfite, and methanol.

7. The fracturing fluid according to claim 1, wherein the alkaline buffer comprises alkaline compounds.

8. The fracturing fluid according to claim 7, wherein the alkaline compounds comprise one or more selected from the group consisting of ammonium and alkaline metal hydroxides, carbonates, and bicarbonates.

9. The fracturing fluid according to claim 8, wherein the alkaline compounds are selected from the group consisting of sodium hydroxide, sodium carbonate, and sodium bicarbonate, and mixtures thereof.

10. The mixed alkaline compounds of claim 9 wherein the ratio of carbonate to bicarbonate may range from about 8:2 to about 2:8.

11. The fracturing fluid according to claim 1, wherein the alpha-hydroxycarboxylic acid delaying agent comprises, the salt of an alpha-hydroxycarboxylic acid, or mixtures of an alpha-hydroxycarboxylic acid and salts of alpha-hydroxycarboxylic acids.

12. The fracturing fluid according to claim 11, wherein the alpha-hydroxycarboxylic acid, or hydroxycarboxylic acid salt, is selected from the group consisting of citric acid, malic acid, glycolic acid, lactic acid, tartaric acid, gluconic acid, glyceric acid, mandelic acid, their salts and mixtures thereof.

13. The fracturing fluid according to claim 1, wherein the delaying agent comprises an ammonium, amine, or alkali metal salt of an alpha-hydroxycarboxylic acid.

14. The fracturing fluid according to claim 13, wherein the ammonium, amine, or alkali metal salt of an alpha-hydroxycarboxylic acid is selected from the group consisting of sodium citrate and ammonium lactate.

15. The fracturing fluid according to claim 1, wherein the zirconium (IV) crosslinking agent comprises any zirconium compound capable of solubilizing in an aqueous polymer solution to release the metal so that gelation takes place under controlled conditions.

16. The fracturing fluid according to claim 1, wherein the zirconium (IV) crosslinking agent is selected from the group consisting of an aqueous solution of a zirconium alpha-hydroxycarboxylic acid salt.

17. The fracturing fluid according to claim 16, wherein the zirconium crosslinking agent is selected from the group consisting of zirconium ammonium lactate, zirconium di or tri ethanolamine lactate, zirconium diisopropylamine lactate, and zirconium sodium lactate salts.

18. The fracturing fluid according to claim 16, wherein the zirconium alpha-hydroxycarboxylic acid salt complex is selected from the group consisting of aqueous solutions of zirconium citrate, zirconium tartate, and zirconium glycolate.

19. The fracturing fluid according to claim 1, wherein the zirconium (IV) crosslinking agent is selected from the group consisting of monoalkylamine zirconium compounds, dialkylamine zirconium compounds, and trialkylamine zirconium compounds.

20. The fracturing fluid according to claim 1, wherein the zirconium (IV) crosslinking agent is selected from the group consisting of a zirconium triethanolamine complex and a diethanolamine complex.

21. A method for formulating an aqueous based zirconium (IV) crosslinked guar fracturing fluid having a pH from about 9 to about 12, comprising the steps of:

placing an aqueous fluid into a suitable mixing device;

adding a stabilizer to the aqueous fluid in an amount from about 1 PPTG to about 50 PPTG of the aqueous fluid;

allowing the stabilizer to dissolve into the aqueous fluid for a first predetermined period;

adding natural guar gum to the mixture in an amount from about 10 PPTG to about 100 PPTG of the aqueous fluid;

mixing the mixture for a second predetermined period;

adding an alkaline buffer to the mixture in an amount from about 1 PPTG to about 40 PPTG of the aqueous fluid;

mixing the mixture for a third predetermined period;

adding an alpha-carboxylic acid delaying agent to the mixture in an amount from about 0.25 PPTG to about 3.75 PPTG of the aqueous fluid;

mixing the mixture for a fourth predetermined period, thereby forming a polymer solution;

adding a zirconium (IV) crosslinking agent in an amount from about 0.1 GPTG to about 5 GPTG of the formulated polymer solution; and

mixing until gelation occurs, thereby producing the fracturing fluid.

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22. The method according to claim 21, wherein the aqueous fluid comprises substantially any aqueous fluid that does not adversely react with one of the constituents of the fracturing fluid, the subterranean formation, and the fluids present therein.

23. The method according to claim 21, wherein the aqueous fluid is selected from the group consisting of fresh water, natural brines, and artificial brines.

24. The method according to claim 23, wherein the artificial brines are selected from the group consisting of such as potassium chloride solutions and sodium chlorides solutions.

25. The method according to claim 21, wherein the stabilizer comprises any free-radical-scavenging compound.

26. The method according to claim 21, wherein the stabilizer is selected from the group consisting of sodium thiosulfate, thiourea, urea, sodium sulfite, and methanol.

27. The method according to claim 21, wherein the alkaline buffer comprises alkaline compounds.

28. The method according to claim 27, wherein the alkaline compounds comprise one or more selected from the group consisting of ammonium and alkaline metal hydroxides, carbonates, and bicarbonates.

29. The method according to claim 28, wherein the alkaline compounds are selected from the group consisting of sodium hydroxide, sodium carbonate, and sodium bicarbonate, and mixtures thereof

30. The method according to claim 21, wherein the delaying agent comprises an alpha-hydroxycarboxylic acid, the salt of an alpha-hydroxycarboxylic acid, or mixtures thereof.

31. The method according to claim 30, wherein the alpha-hydroxycarboxylic acid or alpha-hydroxycarboxylic acid salt is selected from the group consisting of citric acid, malic acid, glycolic acid, lactic acid, tartaric acid, gluconic acid, glyceric acid, mandelic acid, their salts, and mixtures thereof.

32. The method according to claim 21, wherein the alpha-hydroxycarboxylic acid delaying agent comprises an ammonium, amine, or alkali metal salt of an alpha-hydroxycarboxylic acid.

33. The method according to claim 32, wherein the ammonium, amine, or alkali metal salt of an alpha-hydroxycarboxylic acid is selected from the group consisting of sodium citrate and ammonium lactate.

34. The method according to claim 21, wherein the zirconium (IV) crosslinking agent comprises any zirconium compound capable of solubilizing in an aqueous polymer solution to release the metal so that gelation takes place under controlled conditions.

35. The method according to claim 21, wherein the zirconium (IV) crosslinking agent is selected from the group consisting of an aqueous solution of a zirconium alpha-hydroxycarboxylic acid salt.

36. The method according to claim 35, wherein the zirconium alpha-carboxylic acid salt crosslinking agent is selected from the group consisting of zirconium

ammonium lactate, zirconium di or tri ethanolamine lactate, zirconium diisopropylamine lactate, and zirconium sodium lactate salts.

37. The method according to claim 35, wherein the complex of zirconium and an alpha-hydroxycarboxylic acid is selected from the group consisting of aqueous solutions of zirconium citrate, zirconium tartate, and zirconium glycolate.

38. The method according to claim 21, wherein the zirconium (IV) crosslinking agent is selected from the group consisting of monoalkylammonium zirconium compounds, dialkylammonium zirconium compounds, and trialkylammonium zirconium compounds.

39. The method according to claim 21, wherein the zirconium (IV) crosslinking agent is selected from the group consisting of a zirconium triethanolamine complex and a diethanolamine complex.

40. A method of hydraulically fracturing a subterranean zone penetrated by a wellbore, comprising the steps of:

preparing an aqueous based zirconium (IV) crosslinked guar fracturing fluid having a pH from about 9 to about 12, comprising:

a polymer solution, comprising:

an aqueous fluid,

natural guar gum in an amount from about 10 PPTG to about 100 PPTG of the aqueous fluid,

a stabilizer in an amount from about 1 PPTG to about 50 PPTG of the aqueous fluid,

a alkaline buffer in an amount from about 1 PPTG to about 40 PPTG of the aqueous fluid, and

an alpha-hydroxycarboxylic acid delaying agent in an amount from about 0.25 PPTG to about 3.75 PPTG of the aqueous fluid, and

a zirconium (IV) crosslinking agent in an amount from about 0.1 GPTG to about 5 GPTG of the polymer solution;

pumping the fracturing fluid into the subterranean zone via the wellbore;

permitting the fracturing fluid to gel after having substantially traversed the well bore or after having entered the subterranean formation, thereby causing hydraulic fracturing of the subterranean formation.

41. The method according to claim 40, further comprising the steps of:
adding proppants to the fracturing fluid; and
utilizing the fracturing fluid to disperse the proppants throughout the subterranean formation.
42. The method according to claim 40, further comprising the step of adding a breaker to the fracturing fluid to permit the removal of the fracturing fluid from the subterranean formation.
43. The method according to claim 40, wherein the aqueous fluid comprises substantially any aqueous fluid that does not adversely react with one of the constituents of the fracturing fluid, the subterranean formation, and the fluids present therein.

44. The method according to claim 40, wherein the aqueous fluid is selected from the group consisting of fresh water, natural brines, and artificial brines.

45. The method according to claim 44, wherein the artificial brines are selected from the group consisting of such as potassium chloride solutions and sodium chlorides solutions.

46. The method according to claim 40, wherein the stabilizer comprises any free-radical-scavenging compound.

47. The method according to claim 40, wherein the stabilizer is selected from the group consisting of sodium thiosulfate, thiourea, urea, sodium sulfite, and methanol.

48. The method according to claim 40, wherein the alkaline buffer comprises alkaline compounds.

49. The method according to claim 48, wherein the alkaline compounds comprise one or more selected from the group consisting of ammonium and alkaline metal hydroxides, carbonates, and bicarbonates, and mixtures thereof.

50. The method according to claim 48, wherein the alkaline compounds are selected from the group consisting of sodium hydroxide, sodium carbonate, and sodium bicarbonate, and mixtures thereof.

51. The method according to claim 40, wherein the delaying agent comprises an alpha-hydroxycarboxylic acid, the salts of alpha-hydroxycarboxylic acids, or mixtures thereof.

52. The method according to claim 51, wherein the alpha-hydroxycarboxylic acid or alpha-hydroxycarboxylic acid salt is selected from the group consisting of citric

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acid, malic acid, glycolic acid, lactic acid, tartaric acid, gluconic acid, glyceric acid, mandelic acid, their salts, and mixtures thereof..

53. The method according to claim 40, wherein the delaying agent comprises an ammonium, amine, or alkali metal salt of an alpha-hydroxycarboxylic acid.

54. The method according to claim 53, wherein the ammonium, amine, or alkali metal salt of an alpha-hydroxycarboxylic acid is selected from the group consisting of sodium citrate and ammonium lactate.

55. The method according to claim 40, wherein the zirconium (IV) crosslinking agent comprises any zirconium compound capable of solubilizing in an aqueous polymer solution to release the metal so that gelation takes place under controlled conditions.

56. The method according to claim 40, wherein the zirconium (IV) crosslinking agent is selected from the group consisting of an aqueous solution of a zirconium alpha-hydroxycarboxylic acid salt.

57. The method according to claim 56, wherein the zirconium alpha-hydroxycarboxylic acid salt is selected from the group consisting of zirconium ammonium lactate, zirconium di or tri ethanolamine lactate, zirconium diisopropylamine lactate, and zirconium sodium lactate salts.

58. The method according to claim 56, wherein the complex of zirconium and a alpha-hydroxycarboxylic acid is selected from the group consisting of aqueous solutions of zirconium citrate, zirconium tartate, and zirconium glycolate.

59. The method according to claim 40, wherein the zirconium (IV) crosslinking agent is selected from the group consisting of monoalkylammonium

zirconium compounds, dialkylammonium zirconium compounds, and trialkylammonium zirconium compounds.

60. The method according to claim 40, wherein the zirconium (IV) crosslinking agent is selected from the group consisting of a zirconium triethanolamine complex and a diethanolamine complex.

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